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Thickness Dependent Behavior of Photoluminescence of Tris(8-hydroxyquinoline) Aluminum Film

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In situ thickness dependent photoluminescence (PL) measurements of tris(8-hydroxyquinoline) aluminum (Alq_3) film were performed. At the beginning of Alq_3 deposition on the glass substrate, the Alq_3 emission showed a sharp red-shift. Further deposition of Alq_3 resulted slight red-shift, and finally tended to saturated value. The total red-shift of about 12 nm was observed for the Alq_3 film thickness range from 2 to 500 nm. This red-shift was attributed to the change from the 2D to 3D exciton state with increasing Alq_3 film thickness. Meanwhile, the PL intensity of Alq_3 emission increased continuously, and showed a rate change at the initial deposition of Alq_3 due to non-rediative decay of excitons arised from the interaction between excitons and the substrate, and finally tended to saturation with the Alq_3 thickness.

Key words: Tris(8-hydroxyquinoline) aluminum film, Photoluminescence, Red-shift

I. INTRODUCTION

Since the first high efficient organic light emitting diode (OLED), which used the aromatic diamine as the hole transport layer and tris(8-hydroxyquinoline) aluminum (Alq_3) as the electron transport/emission layer, was demonstrated by Tang *et al.* [1,2], Alq_3 is commonly used as the electron transport and/or emitting layer in OLEDs for its efficient luminescence and relative stability. Recently, in order to get higher efficient and stable devices, many efforts have been made on the device optimization, such as high luminescence efficiency, operation stability and color tuning [3-6].

As we know, the light absorption and emission behavior of organic semiconductors are different from those of inorganic semiconductors. In general, the excitons in organic semiconductors are highly localized, e.g. the charge-transfer (CT) excitons are localized within a few molecules, while the Frenkel excitons are almost localized within one molecule. The localization of excitons in organic semiconductors consequently determines the properties of their luminescence. The systemic photoluminescence (PL) study of organic semiconductors can obviously explore the properties of exciton states and their decay behavior. As a useful tool, PL spectroscopy measurements are extensively used to study the intrinsic properties, such as exciton states, and energy transfer process etc. With a device structure of ITO/TPD/Alq_3:DCJTB/LiF/Al, Zhao *et al.* [7] have investigated the energy transfer behavior from Alq_3 to

DCJTB by using PL spectroscopy, and the DCJTB peak position shifted about 30 nm due to self polarization. Jiang *et al.* [8] reported PL spectroscopy measurements for Rhodamine 6G in low melting temperature glass, and the red-shift of the Rhodamine 6G emission was observed. The optical properties of Alq_3 were also investigated by a few research groups [9-12]. For example, based on a device structure and PL measurements, Yang *et al.* [9] reported a red-shift of Alq_3 emission from powder to thin film. They owned the peak shift to the difference of molecular space structure between the amorphous thin film and polycrystalline powder. However, the detailed understanding of the intrinsic optical properties of Alq_3 thin film and the dependence of Alq_3 emission on film thickness are still demanded. In this paper, we reported our in situ photoluminescence (PL) spectroscopy measurements of Alq_3 film, and the results showed clearly the thickness dependent variations on both the PL intensity and the peak position of Alq_3 emission.

II. EXPERIMENTAL

The experiments were performed in a high-vacuum (HV) multilayer growth system with a base pressure better than 5×10^{-6} Pa. The system were equipped a few organic and metal evaporators, a sample holder with heater, and an optical fiber for outputting the optical signals from vacuum for PL measurements.

Thin films of Alq_3 were prepared by thermal evaporation of Alq_3 onto a glass substrate (slide). The glass substrate was cleaned by conventional chemical method first, and then by preheating for removing the contaminations in the HV chamber. Alq_3 was deposited from

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a resistance-heating (tantalum boat) evaporator. Alq$_3$ powder was purified by preheating at about 150 °C, and deposition was done at a temperature of about 180°C. The steady deposition rate was about 1.5 nm/min, and the substrate was held at room temperature. The thickness of Alq$_3$ film was monitored and measured with quartz oscillator.

The source light of Neoark DPS-5004 diode laser (405 nm, 35 mW) for PL measurements was directly delivered through a glass window to the sample. The PL spectra were collected with the USB2000 Fiber Optical Spectrometer (Ocean Optics Inc.).

III. RESULTS AND DISCUSSION

Alq$_3$ is an organic fluorescence material with high quantum efficiency. There exist triplet and singlet exciton states, and the luminescence of Alq$_3$ originates from the radiative decay of the singlet state. Figure 1 shows the typical PL spectra of the Alq$_3$ film deposited on the glass slide at room temperature. It can be clearly seen from the inset of Fig.1 that there is a visible PL peak at about 524 nm with the Alq$_3$ film thickness of about 1 nm, approximately one molecular monolayer. Obviously, the PL intensity of the Alq$_3$ film increases with film thickness, and the position of the Alq$_3$ emission peak has a red-shift. The thickness dependences of the PL intensity and peak position are displayed in Fig.2 and Fig.3 respectively. In order to distinctly depict the variation of PL intensity in the low thickness range, the parameter of thickness in Fig.2(b) is adopted with logarithmic coordinates. With the Alq$_3$ film thickness increasing from 2 nm to 500 nm, the PL intensity shows an increase by a factor of 20 and the peak position shifts from about 524 nm to 536 nm, the total red-shift is about 12 nm.
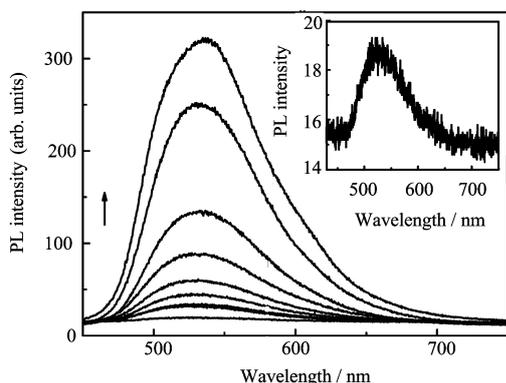

FIG. 1 PL spectra collected for Alq$_3$ film at different thickness. Along the arrow direction, the thicknesses in turn are 2, 8, 12, 16, 22, 50, 100, 200, 500 nm, the inset shows the PL spectrum of 1 nm thick Alq$_3$ film.

As shown in Fig.2(a), the PL intensity of the Alq$_3$ emission increases sharply at the initial deposition of Alq$_3$, and tends to a saturated value with the Alq$_3$ film in the high thickness range. The increase of the PL
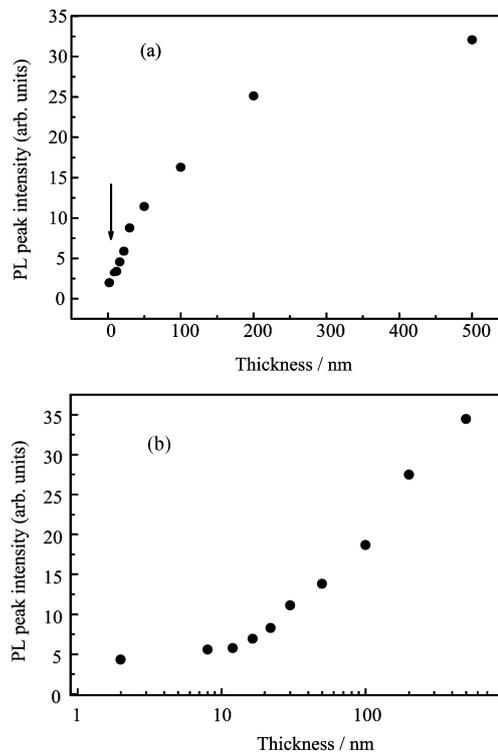

FIG. 2 (a) Thickness dependence of PL peak intensity as a function of the Alq$_3$ film thickness for Alq$_3$ film. (b) The plot with semi-logarithmic scale, shows the rate change at the initial deposition of Alq$_3$.
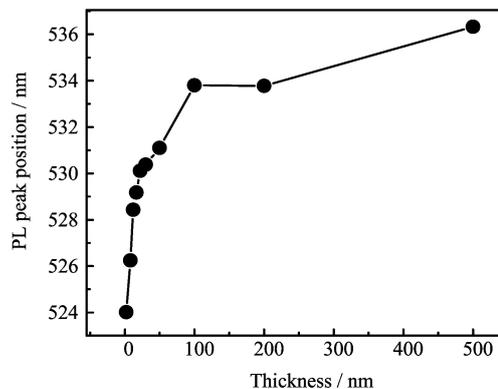

FIG. 3 Thickness dependence of PL peak position as a function of the Alq$_3$ film thickness for Alq$_3$ film.

intensity with thickness of the film is due to the fact that more molecules are involved in photoluminescence with thicker film. When the thickness of the film (in the high thickness range) reaches to a certain point, the PL intensity should approach a saturated value since the penetration of the excitation laser source into the Alq$_3$ film (bulk) should be limited. However, the PL intensity increases with the film thickness continuously and it shows a rate deference, as indicated by the arrow in Fig.2(a) (we can also clearly see this rate change in Fig.2(b)), i.e., the increasing rate is lower at the initial deposition of Alq$_3$ than that at the late stage. This low increasing rate at the initial deposition of Alq$_3$ could

be related to the high probability of nonradiative decay caused by interaction of excitons with substrate [13].

Alq$_3$ thin films grown with the substrate temperature at room temperature should be in the amorphous state [14], and the excitons are more like Frenkel excitons. Interestingly, as shown in Fig.3, the Alq$_3$ emission peak also shows a sharp red-shift at the initial deposition of Alq$_3$, and approaches a saturation value upon the film thickness in the high thickness range. This red-shift can be attributed to the change from the 2D exciton state (surface component) to the 3D exciton state (bulk component). It is known that the lowest electronic excitation of the outmost monolayer (2D exciton state) has blue-shift with respect to the exciton of the bulk in organic systems [15], and the decay of the monolayer exciton is purely radiative with a small contribution of relaxation to the bulk. Considering the excitons, as "small radius" excitons, being the Frenkel or CT excitons, and with the surface and bulk components, the red-shift of the PTCTA singlet exciton line with increasing layer thickness was well simulated [15]. Apparently, for a thinner Alq$_3$ film, the surface component is dominant, and the singlet exciton is much like a 2D one, which leads to Alq$_3$ emission at the blue side, while for the thicker and smoother film with lower surface area, the contribution from the bulk (the 3D exciton) becomes dominant, which will result in a red-shift of Alq$_3$ emission peak.

It is known that reduction of the dimensions of organic semiconductors, for example, changing the organic system from 3D to 2D, and reducing the size of organic nanoparticles, will lead to exciton confinement, giving rise to a blue-shift of the related emissions. Actually, the adsorption and emission spectra measurements on the PDDP nanoparticles system showed a size effect [16], i.e., the emission related to the extended charge-transfer (CT) excitons shifts to high-energy side with decreasing nanoparticle size due to exciton confinement. In the present case of Alq$_3$ film, the higher energy of Alq$_3$ emission at the initial deposition of Alq$_3$ (2D excition state) could also related to this quantum confinement. However, the dielectric environment of a single molecular (2D) film is different from the bulk due to absence of neighboring molecules, which will lead to a shift of the related emissions. Also with thinner Alq$_3$ film, the charge transfer at the interface due to the interaction between Alq$_3$ and the substrate will modify the Alq$_3$ electronic structure, giving rise to a change in Alq$_3$ emission. With emission spectra measurements based on device structure, Huang *et al.* [17] reported a red-shift of Alq$_3$ emission in different dielectric environment between outermost monolayer and the bulk.

IV. CONCLUSIONS

We carried out in situ photoluminescence spectroscopy measurements on Alq$_3$ thin film deposited on glass substrate. Upon deposition of Alq$_3$ on the glass substrate, the PL intensity of Alq$_3$ emission increased continuously with the film thickness, and finally tended to a saturated value, while PL peak position showed a red-shift of about 12 nm for the Alq$_3$ film thickness range from 2 to 500 nm. The thickness dependence of the PL intensity for Alq$_3$ emission can be understood with the radiative decay of excitons in Alq$_3$ film and the non-radiative decay of excitons caused by the interaction of excitons with the substrate. The thickness dependence of the red-shift for Alq$_3$ emission, especially the sharp red-shift at the beginning of Alq$_3$ deposition, was attributed to the change from the 2D to 3D excition state.

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